

Origin of Superconductivity in Fullerenes Still a Mystery

Soccer-ball-shaped molecules called fullerenes can carry electricity with no energy loss – a phenomenon called superconductivity – at temperatures below -387 degrees Fahrenheit. To increase this temperature, and thus make fullerenes' use more convenient for applications in electronics, drug delivery, and nanotechnology, scientists have long assumed that they simply needed to introduce larger and larger atoms inside fullerene compounds.

In the April 5, 2002 issue of *Science*, however, scientists working at the NSLS report an unexpected result: When they added molecules of bromoform and chloroform to a fullerene compound, the resulting compound changed its structure.

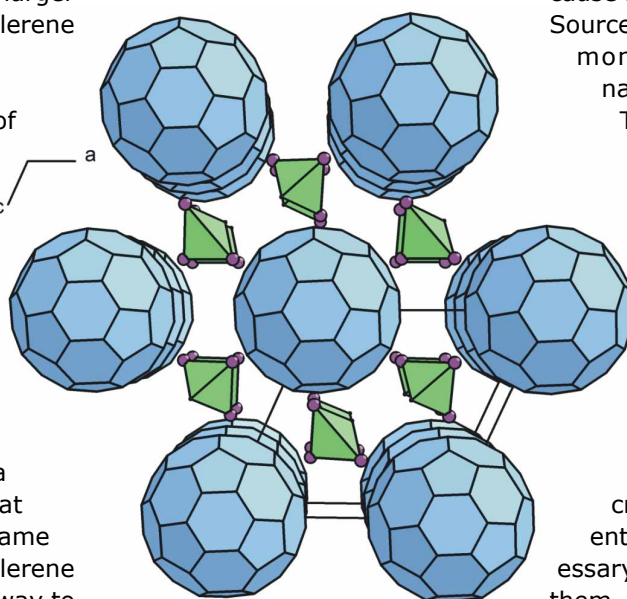
This result contradicts a widely held assumption that the structure remains the same in both pure and "mixed" fullerene compounds, and paves the way to a new understanding of how superconductivity works in these compounds.

"The theory of superconductivity in fullerenes is still too simple," says Robert

Dinnebier, a physicist at the Max Planck Institute for the Physics of Solids in Stuttgart, Germany, one of the world leading labs in materials science. "Our finding means that the increase in temperature seems to be due to other causes than just an increase in spacing between the fullerene molecules."

Dinnebier and his colleagues came upon this new result while attempting to understand findings published a month earlier in *Science*.

A team of physicists led by physicist Hendrik Schoen, of both Bell Laboratories in Murray Hill, New Jersey and the University of Konstanz in Germany, had, for the first time, reported that when chloroform and bromoform were added to fullerene compounds, their superconducting temperature increased dramatically.



Structure of a fullerene crystal (blue) with chloroform molecules (green/purple) inserted within the lattice. Although the structure was expected to be cubic, Dinnebier and his coworkers found that it was, in fact, hexagonal, as shown in the figure.

"When this work was published, we immediately thought it would be very interesting to look at the structure," Dinnebier says. Detailed structural studies of the spacing between fullerenes might explain the increase in temperature, the scientists assumed. "Within two weeks, we prepared the material and sent it to the NSLS," Dinnebier says.

At the NSLS, Dinnebier's collaborators Peter Stephens, a physicist

at the State University of New York at Stony Brook, and his doctoral student, Ashfia Huq, set up an experiment to look at the structure of the chloroform- and bromoform-based fullerenes.

"When Robert [Dinnebier] told me that the material would be available, I was very excited," Stephens says. "We had to act quickly, because this was just before the Light Source would shut down for two months for routine maintenance."

To reveal the material's crystalline structure, the scientists used a technique called powder x-ray crystallography. They projected x-rays produced by the NSLS toward a powder of tiny crystals of the compound. Then, they determined its structure by looking at how the x-rays scattered off the crystals. In one week, the scientists had produced the necessary data and started analyzing them.

By measuring the distances between the fullerene molecules in three directions (up-down, left-right, and forward-backward), the researchers found that the expansion of the molecules due to the bromoform or chloroform mainly takes place in one direction, instead of three directions, as predicted. Surprised at first, the scientists later realized that the structure of the compounds was different from what was theoretically predicted.

In a fullerene compound, the molecules form a series of connected cubes in three directions. The molecules are on the corners of each

cube, and at the center of the cube's faces.

Schoen's group expected that when bromoform or chloroform molecules are inserted inside a fullerene compound, they would sit in between the fullerene molecules. In this way, the fullerene molecules would be pushed apart similarly in the three directions, Dinnebier explains.

The new results show that the fullerene compounds with chloroform or bromoform were no longer cubic. Instead, the fullerene molecules form six-sided hexagonal shapes. The compound is made of parallel planes, each containing a series of connected hexagons. "The chloroform and bromoform molecules sit in between the planes, pushing the fullerene molecules apart only in the direction perpendicular to the planes," Dinnebier says.

While these results give a clearer picture of how a fullerene com-

pound can be modified by adding chloroform or bromoform, they still do not provide answers to what causes the increase of the superconducting temperature. One possibility is that when chloroform or bromoform molecules are added to the fullerene compound, their electrons add to the ones already existing in the compound. The collective motion of all the electrons then creates heat that increases the temperature.

According to the theory, the number of electrons would have to increase by 25 to 35 percent to explain the measured superconducting temperature. However, theoretical physicist Olle Gunnarsson, a member of the Stuttgart team, showed that, in a hexagonal structure, the number of electrons increases by, at most, 10 percent. Another possibility, suggested by Dinnebier and his colleagues in their article, is that the chloroform and bromoform molecules may play a role through interactions between their electrons, but this

hypothesis has not yet been tested. "Understanding the causes of superconductivity and the origin of the temperature below which it operates are still elusive," Stephens says. "But these results form the basis for uncovering how fullerene-based compounds generate superconductivity at the atomic level."

"This kind of research is a beautiful advertisement for the way the NSLS works," he adds. "At the NSLS, like many other synchrotron sources, it is curiosity-driven scientists, not committees, that make the decisions to schedule most of the experiments. We owe the success of this work to this well-established culture at the NSLS."

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Robert E. Dinnebier, et al., "Structure of Haloform Intercalated C₆₀ and Its Influence on Superconductive Properties," *Science*, **296**, 109 (2002). -Patrice Pages